The role of composition and surface area variability in ice nucleation, and how to get rid of it

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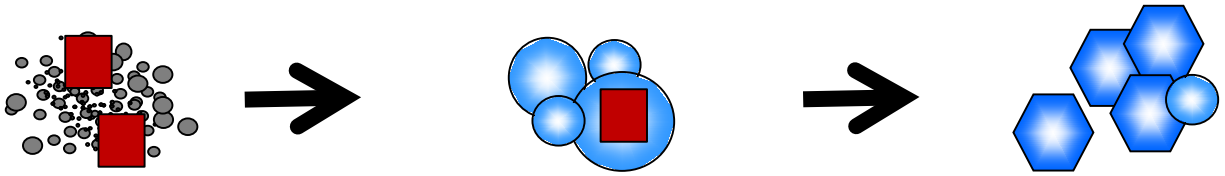
Special thanks to Ben Murray and Tom Whale

Immersion Ice Nucleation



Soluble and Insoluble Aerosol Ice Nuclei (INP) Mostly dust, soot, and biological material

Immersion Freezing

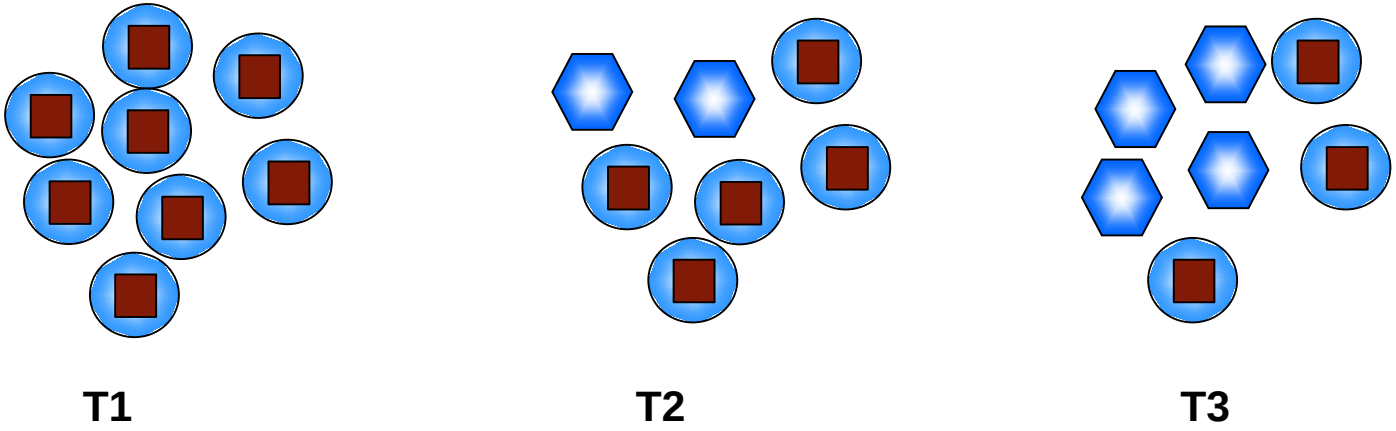
Ice crystal population

- INP completely immersed
- Thermodynamic equilibrium
- Could happen at RH<100%

- Plays a very important role in the evolution of Arctic and Convective clouds. May affect climate sensitivity (Tan et al. 2016).

- Parameterized by estimating ice nucleation efficiencies from laboratory data either in the form of active site density, or by constraining nucleation theories

Immersion Ice Nucleation



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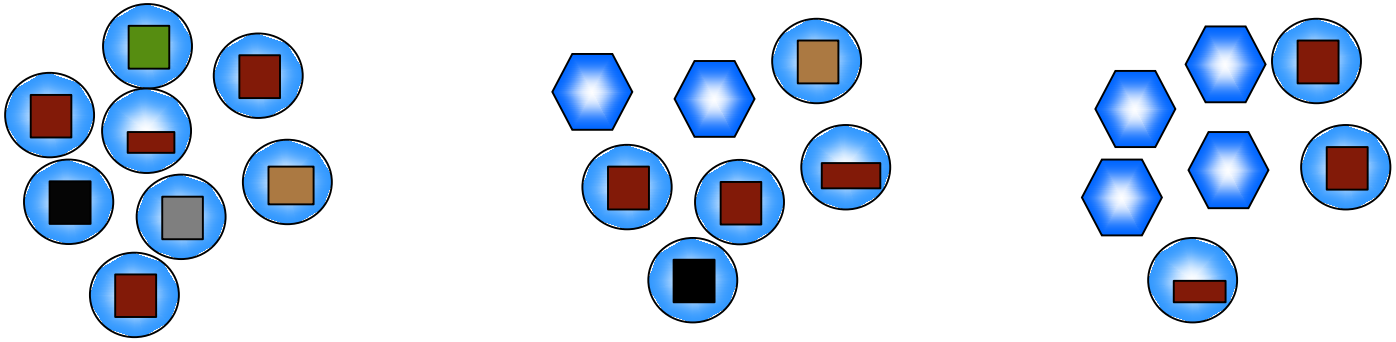

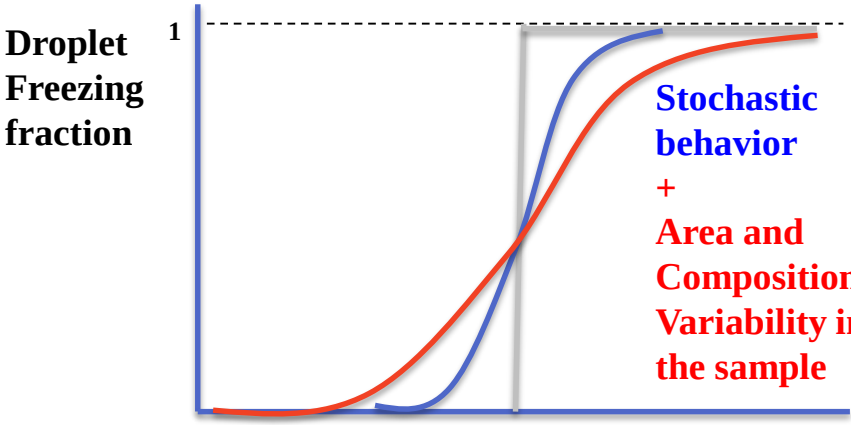

Active site density

Nucleation rate

+ Bias

Dealing with variability

- Singular approach: Typically neglected.
  - Variability in the sample is about the same as in the target population.

- Stochastic approach: Contact angle distribution P(θ) for the population (and sometimes for each particle).
  - Assumes CNT as correctly describing the underlying physical nucleation mechanism.
  - Cannot be used to validate nucleation theories.
  - P(θ) is not a fundamental property of the material as it carries information on sample variability

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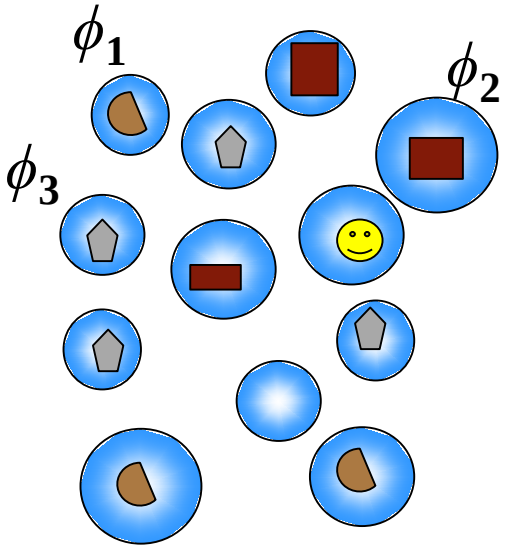
How significant is the bias in active site density/nucleation rate introduced by neglecting variability?

How to remove it without assuming an specific mechanism (e.g., CNT)?

Modeling Variability



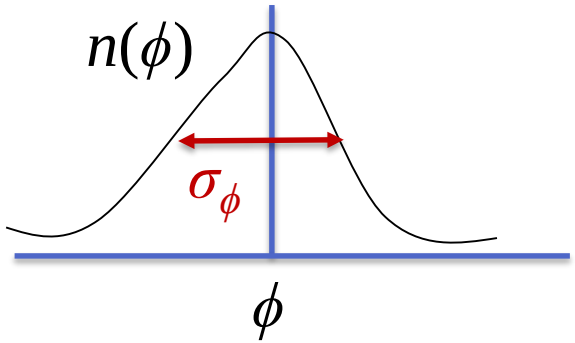
ϕ = area*active site density = J*area

ϕ ~ =# active sites per droplet

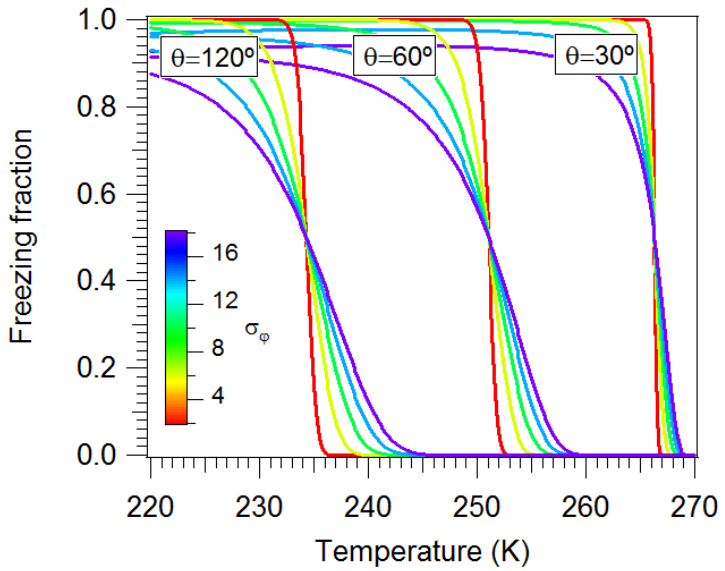
Freezing fraction = $f_f = 1 - \int_0^\infty e^{-\phi} n(\phi) d\phi.$

$$f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)$$

Laplace transform of $n(\phi)$ calculated at the mean ϕ



***n*(ϕ) is likely lognormal**



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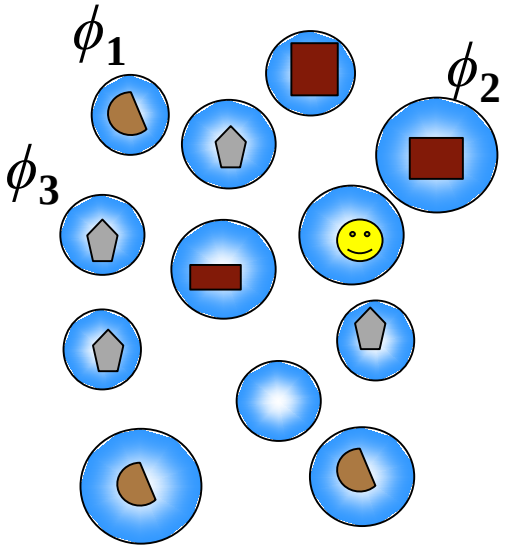

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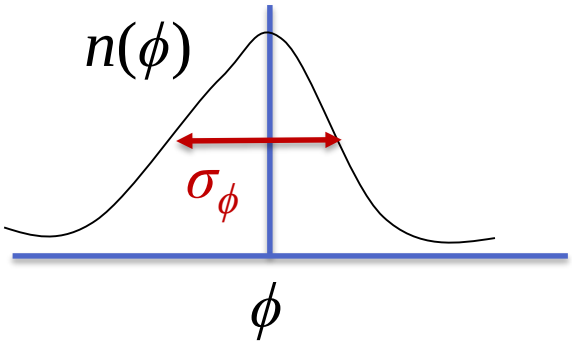


***n*(ϕ) is likely lognormal**

$\sigma_\phi \rightarrow 0,$ $\quad \bar{\rho}_{as,app} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$

Apparent active site density

Using Synthetic Data to Estimate the Effect of Variability

1- Use nucleation theory to find an "equivalent" active site density. This is the "true" value,

$$\rho_{as,true} \equiv \int_0^t J\, dt'$$

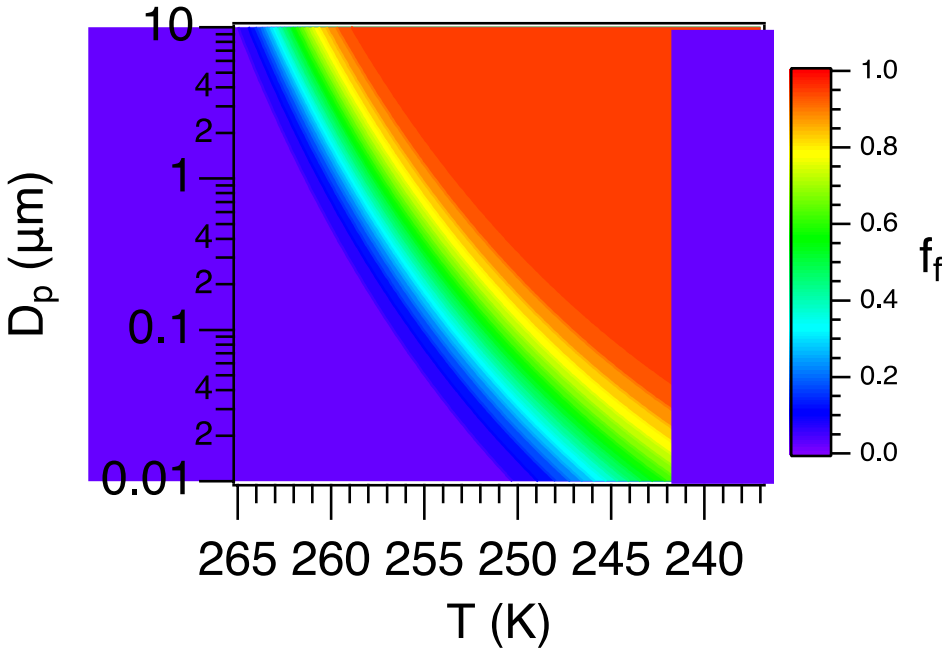
2- Find freezing fraction for a given σ_ϕ,

$$f_f = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)$$

3- Compare $\rho_{as,\,true}$ Vs. $\rho_{as,\,app}$,

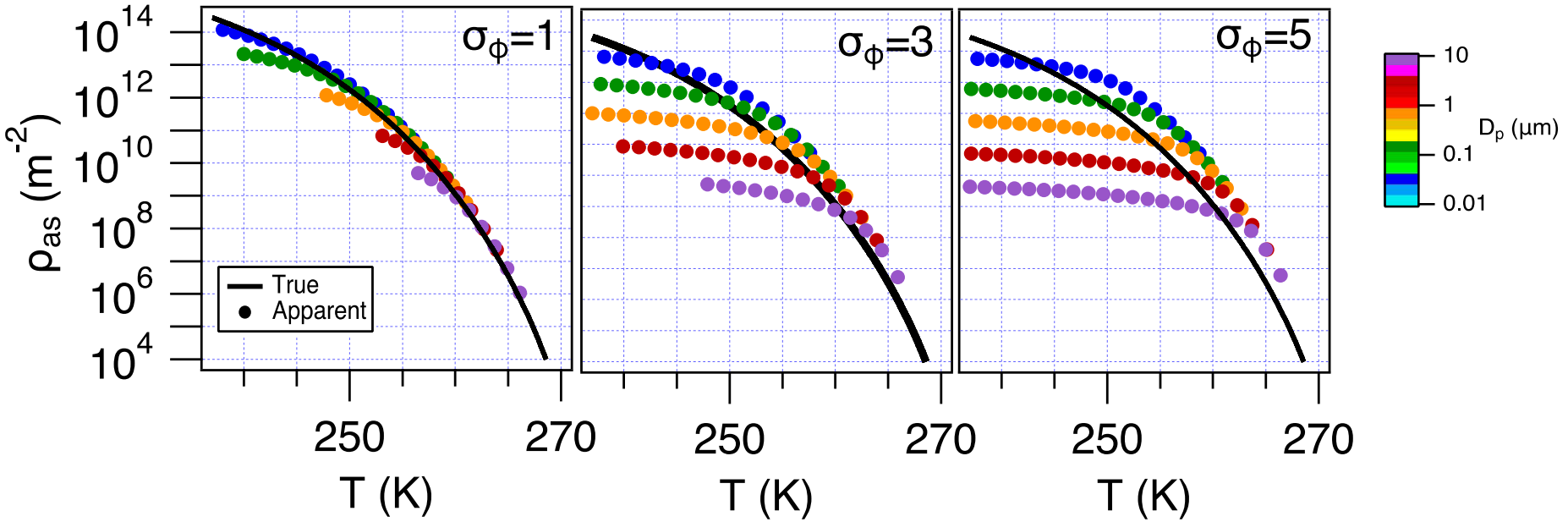
$$\bar{\rho}_{as,app} = -\frac{\ln(1 - f_f)}{\bar{s}_p}$$

Droplet freezing fraction for Microcline, σ_ϕ =2



Barahona ACP 2018, Ickes et al. ACP, 2017.

How much does variability matter?



Increasing dispersion

$$\bar{\rho}_{\mathrm{as,app}} = -\frac{\ln(1-f_{\mathrm{f}})}{\bar{s}_{\mathrm{p}}}$$

$\rho_{as,\,app}$ may underestimate the actual active site density by several orders of magnitude, and, it is not independent of surface area

Eliminating the bias

We don't know σ_ϕ in advance

$$f_\mathrm{f} = 1 - \mathcal{N}(\bar{\phi}, \sigma_\phi)$$

$$\bar{\rho}_\mathrm{as} = \frac{1}{\bar{s}_\mathrm{p}} \mathcal{N}^{-1}(1 - f_\mathrm{f})$$

Invert
(Quite difficult)

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$$\bar{\rho}_\mathrm{as} = \frac{1}{\bar{s}_\mathrm{p}} \mathcal{N}^{-1}(1 - f_\mathrm{f})$$

$$\frac{\partial f_\mathrm{f}}{\partial T} = -\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}\bar{\phi}} \frac{\partial \bar{\phi}}{\mathrm{d}T}$$

$$\frac{\partial f_\mathrm{f}}{\partial \ln \bar{s}_\mathrm{p}} = -\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}\bar{\phi}} \frac{\partial \bar{\phi}}{\mathrm{d}\ln \bar{s}_\mathrm{p}}.$$

$$\frac{\partial \bar{\phi}}{\partial T} - \alpha \frac{\partial \bar{\phi}}{\partial \ln \bar{s}_\mathrm{p}} = 0 \quad \Rightarrow \quad \frac{\mathrm{d}g}{\mathrm{d}T} - \alpha g = 0 \quad \Rightarrow \quad \ln \frac{g}{g_o} = \int \alpha \mathrm{d}T$$

$\phi = s_p * \rho_{as} = s_p * g$

$$\bar{\rho}_\mathrm{as} = -\frac{\ln(0.5)}{\bar{s}_\mathrm{p}} \exp\left(\int_{T_{50}}^{T} \alpha \mathrm{d}T \right) \qquad \alpha = \frac{\partial f_\mathrm{f}}{\partial T} \Big/ \frac{\partial f_\mathrm{f}}{\partial \ln \bar{s}_\mathrm{p}}.$$

T_{50} = Temperature at $f_f = 0.5$
s_p = mean surface area per droplet

Bias-Free Ice Nucleation Efficiency

$$\bar{\rho}_{\mathrm{as}} = -\frac{\ln(0.5)}{\bar{s}_{\mathrm{p}}} \exp\left(\int_{T_{50}}^{T} \alpha \mathrm{d}T\right)$$

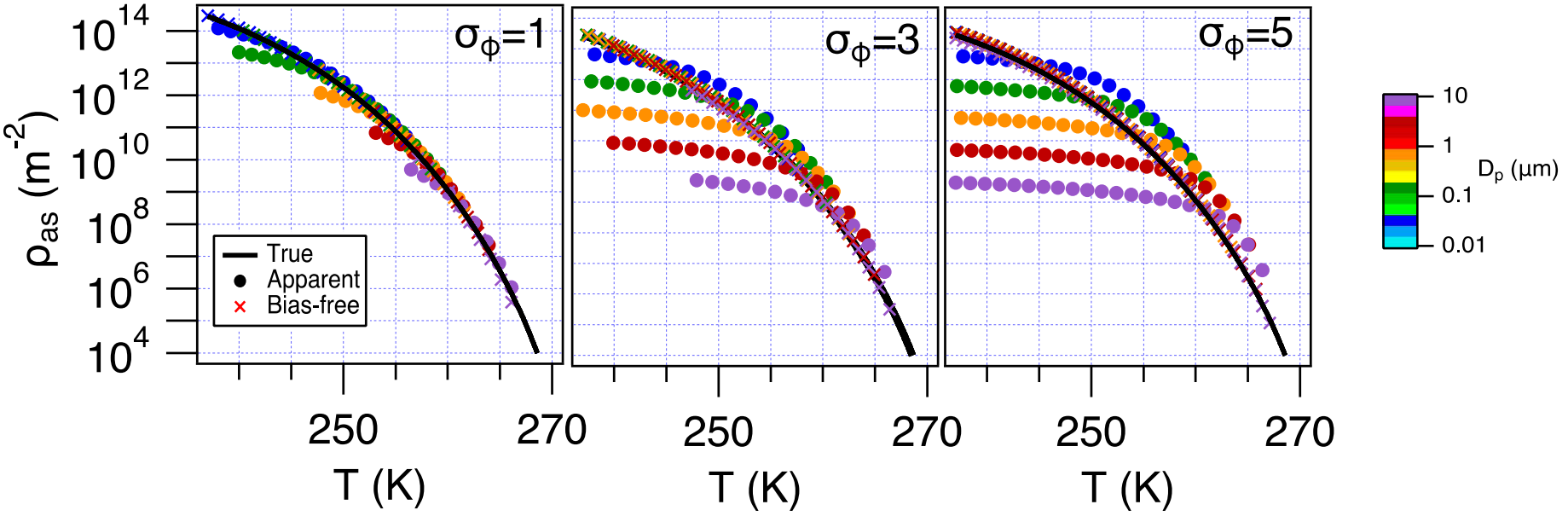
$$\alpha = \frac{\partial f_{\mathrm{f}}}{\partial T} \Big/ \frac{\partial f_{\mathrm{f}}}{\partial \ln \bar{s}_{\mathrm{p}}}.$$

ρ_{as} =Active site density
T_{50} = Temperature at f_f = 0.5
s_p= mean surface area per droplet

By performing droplet freezing measurements as a function of both particle surface area and temperature, the intrinsic nucleation efficiency of a material can be obtained.

Barahona, 2020, Submitted

How much does variability matter?



Increasing dispersion

The bias-free estimate always overlaps with the true value. Independent of variability. Corresponds to the actual efficiency.

$$\bar{\rho}_{\mathrm{as,app}} = -\frac{\ln(1 - f_{\mathrm{f}})}{\bar{s}_{\mathrm{p}}}$$

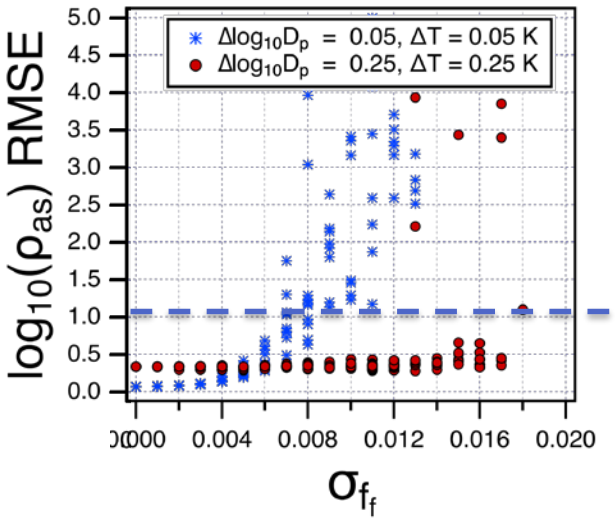
What about the real world?

$$\bar{\rho}_{\mathrm{as}} = -\frac{\ln(0.5)}{\bar{s}_{\mathrm{p}}} \exp\left(\int_{T_{50}}^{T} \alpha \mathrm{d}T\right)$$

$$\alpha = \frac{\partial f_{\mathrm{f}}}{\partial T} \Big/ \frac{\partial f_{\mathrm{f}}}{\partial \ln \bar{s}_{\mathrm{p}}}.$$

Assumptions:

1. T_{50} is known
2. The partial derivatives of f_f can be accurately calculated



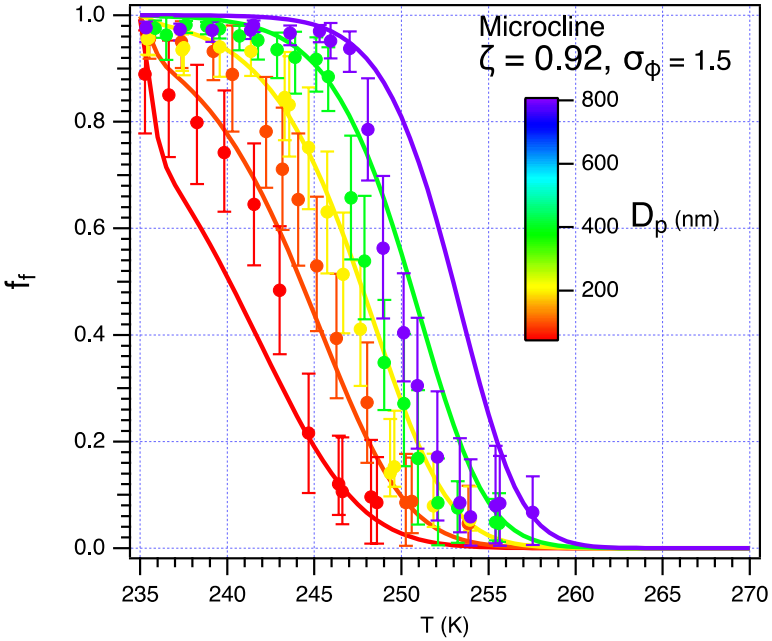
Random Error in f_f

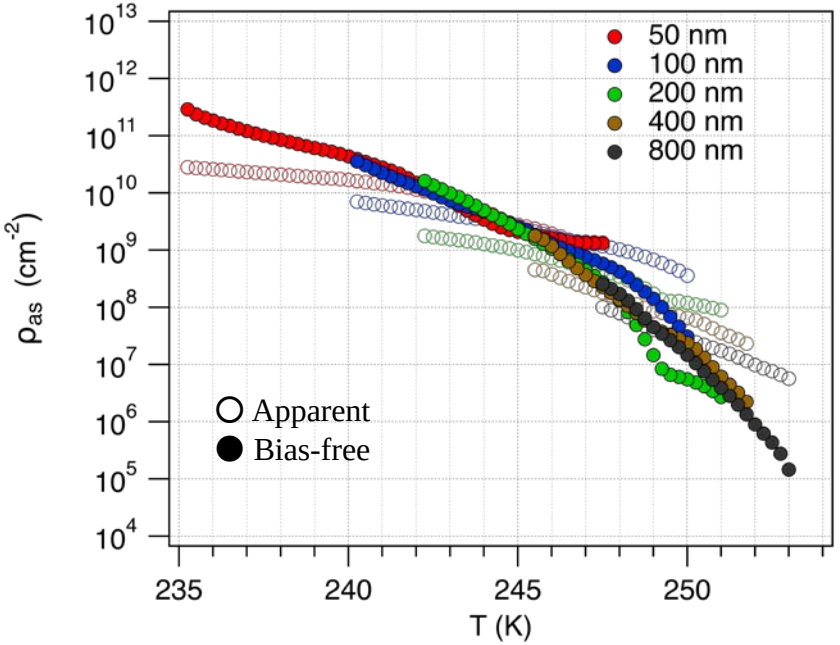
As a rule to keep the RMS error under one order or magnitude:

- **$\Delta T \sim 0.5$ K**
- **$\Delta \log_{10} D_p \sim 0.5$**
- **$\sigma_{ff} < 5$ %**

- Smooth spectra may accommodate larger error

Application to Existing Data Sets





*Data has been interpolated to 0.25 K
Estimated error is about one order of magnitude

$$\bar{\rho}_{\mathrm{as}} = -\frac{\ln(0.5)}{\bar{s}_{\mathrm{p}}} \exp\left(\int_{T_{50}}^{T} \alpha \mathrm{d}T\right)$$

$$\bar{\rho}_{\mathrm{as,app}} = -\frac{\ln(1-f_{\mathrm{f}})}{\bar{s}_{\mathrm{p}}}$$

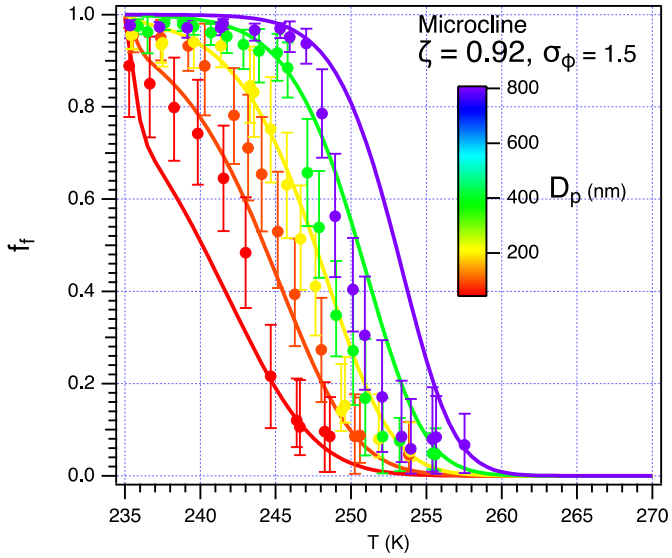
The bias free estimate shows a more consistent trend than the apparent value

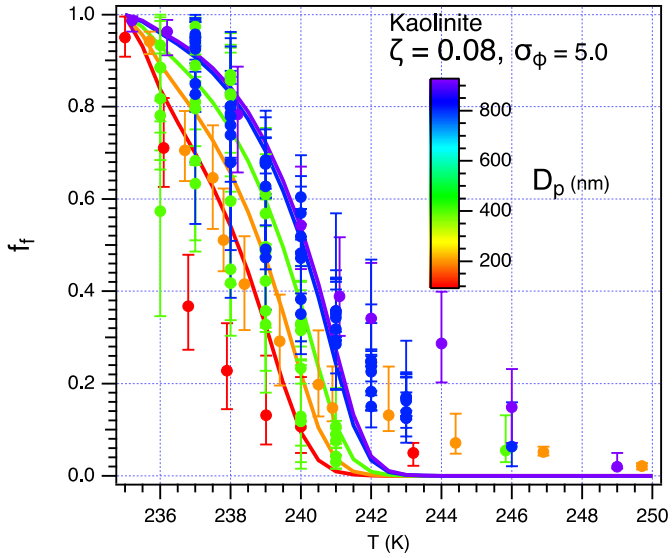
Ickes et al. ACP, 2017; Barahona, 2020, Submitted

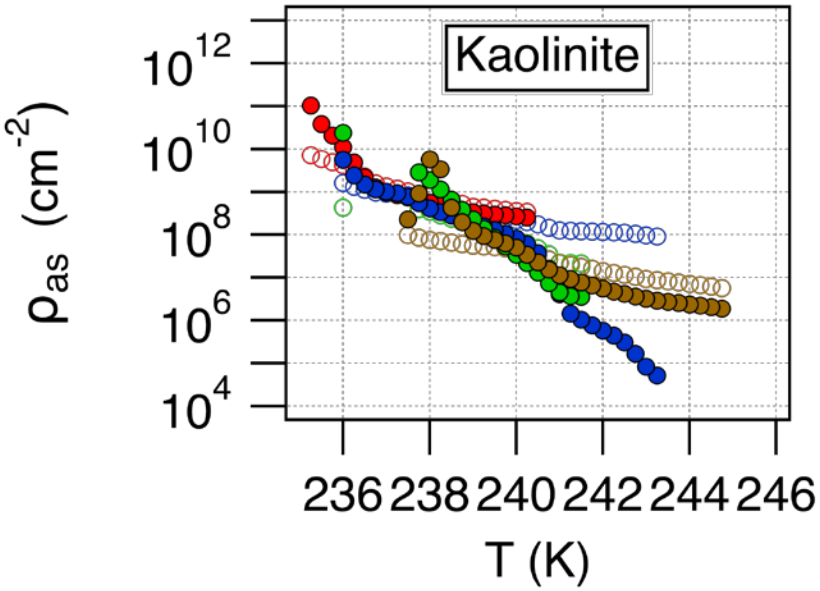
Conclusions

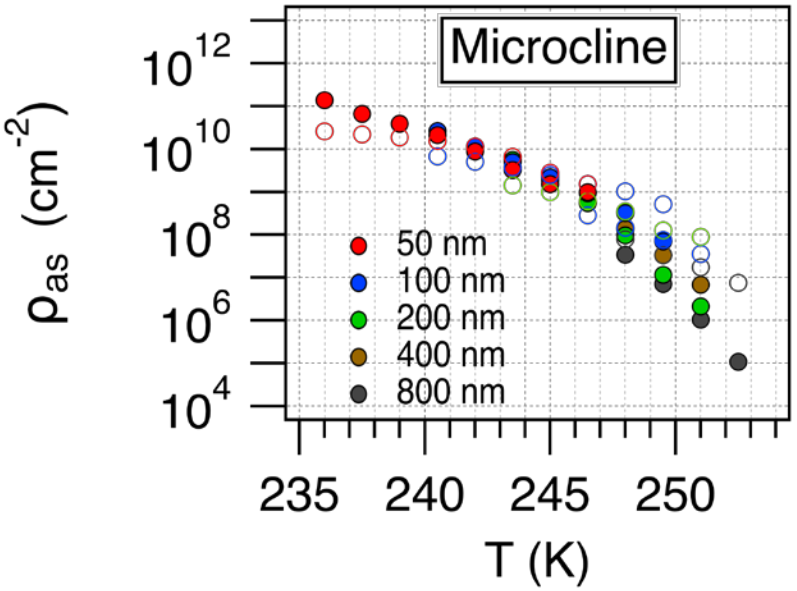
- Ice nucleation active site densities and nucleation rates obtained from droplet freezing experiments may be biased because variability is neglected.
- Such as bias may be significant reaching several orders of magnitude in parameterized active site density. It may translate to about 40% error in freezing fraction (~3 K in freezing threshold) when used in models.
- A method is introduced that for the first time allows to estimate the intrinsic ice nucleation efficiency of a give material. In many cases the accuracy of current experimental techniques is enough to improve estimates.
- The proposed method amounts to a distinction between the “freezing rate” and the actual nucleation rate of a material. It allows the validation of nucleation theories.

THANKS!









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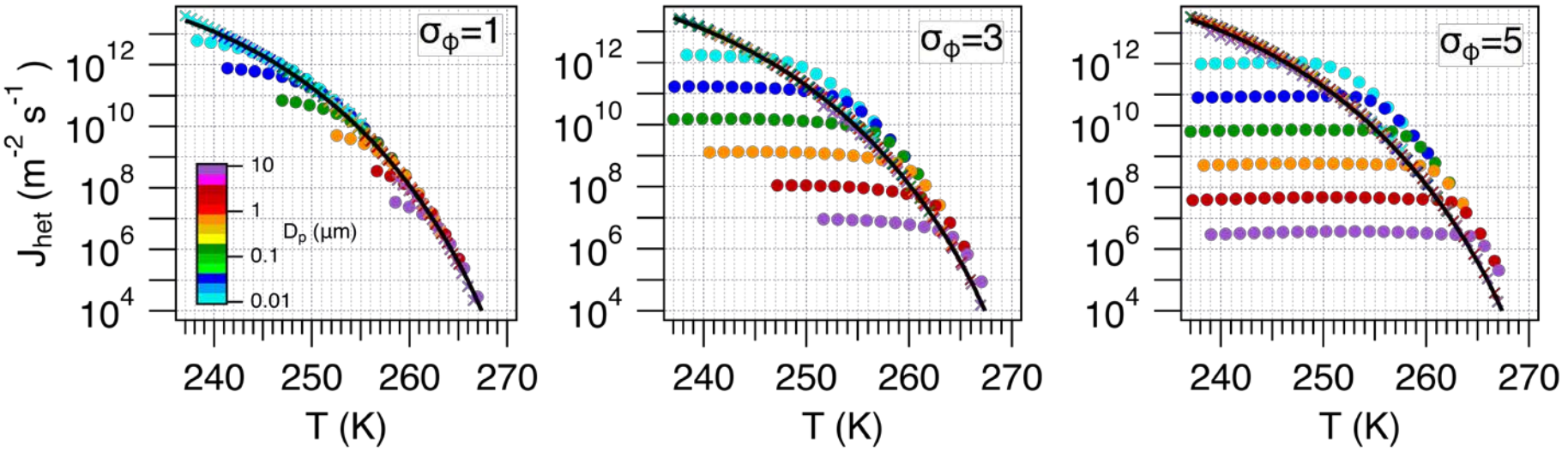
σϕ=1
σϕ=3
σϕ=5
J_{het} (m^{-2} s^{-1})
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10
1
0.1
0.01
D_p (μm)
240
250
260
270
T (K)